
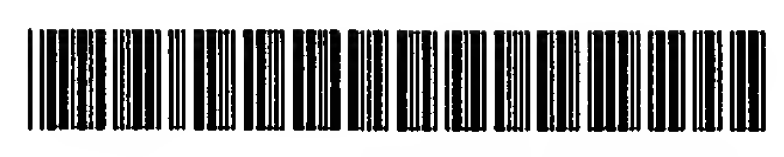


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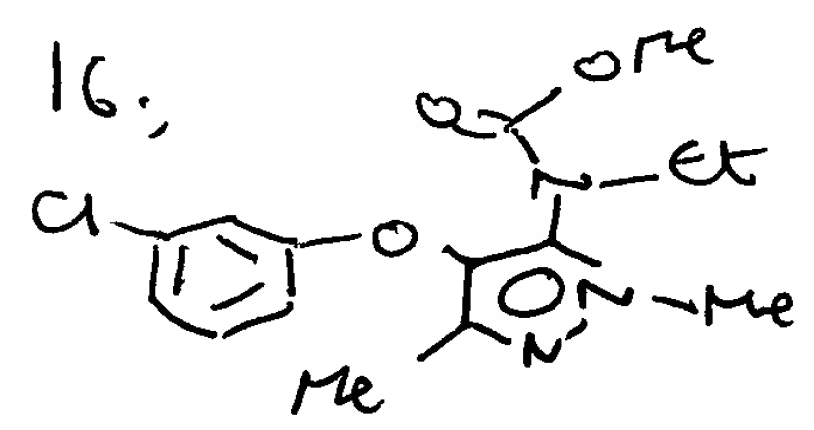
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⑫ **EUROPEAN PATENT APPLICATION**

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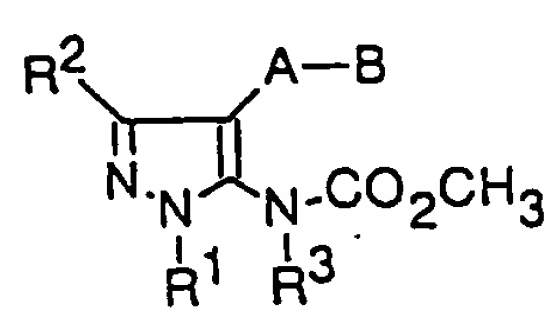
Inventor: **Katsurada, Manabu, Mitsubishi Chemical Corporation**
c/o Yokohama Res. Center,
1000, Kamoshida-cho
Aoba-ku,
Yokohama-shi,
Kanagawa-ken (JP)
— **— Hirofumi, Mitsubishi**



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⑤⑦ An N-pyrazolyl carbamate derivative represented by the general



(I)

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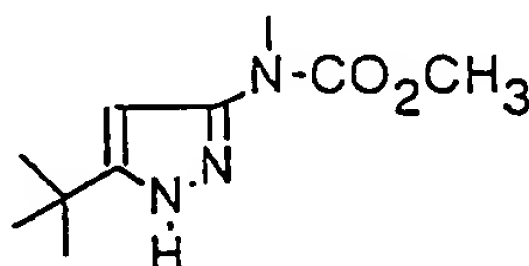
wherein R¹ and R² independently indicate a hydrogen atom or a C₁-C₄ alkyl group; R³ is a hydrogen atom, a C₁-C₄ alkyl group, a C₂-C₅ alkynyl group, a C₂-C₄ alkylthioalkyl group or a C₂-C₄ alkoxyalkyl group; A is -O-, -C(O)-, -OCH₂-, -CH₂O-, -CH₂S-, -C≡C-, -CH=CH-, -CH₂CH₂-, -CH₂ON=C(R⁴)- or -CH=NOC(R⁴)(R⁵)- (where in R⁴ and R⁵ independently indicate a hydrogen atom or a C₁-C₄ alkyl group); and B is a hydrogen atom, an optionally substituted aryl group or an optionally substituted heterocyclic group, an agricultural/horticultural fungicide containing the N-pyrazolyl carbamate derivative as an active ingredient, and a production intermediate thereof are disclosed.

FIELD OF THE INVENTION

The present invention relates to a novel N-pyrazolyl carbamate derivative and an agricultural/horticultural fungicide containing the same as an active ingredient.

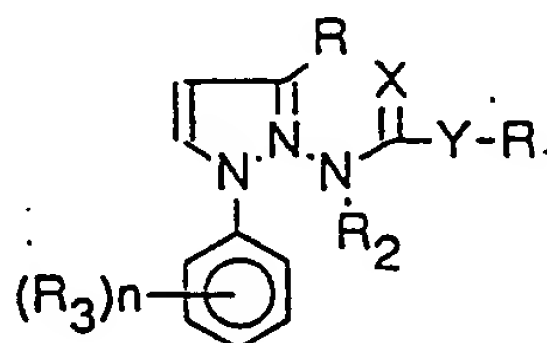
BACKGROUND OF THE INVENTION

It has hitherto been known that a certain N-pyrazolyl carbamate derivative has a biological activity such as herbicidal effect. For example, in EP129830, there is described a compound of the formula:



as a compound having a herbicidal activity.

In DE3423582, there is also described a compound of the formula:



wherein R is a cyano group or an alkoxy carbonyl group; R₁ is an alkyl group or an aryl group; R₂ is a hydrogen atom or a group of -C(X)YR₁; and X and Y indicate an oxygen atom or a sulfur atom, as a compound having a herbicidal activity.

However, these compounds are not necessarily suitable as an agricultural/horticultural fungicide at present.

OBJECTS OF THE INVENTION

The present inventors have intensively studied about the N-pyrazolyl carbamate derivative. As a result, it has been found that, a N-pyrazolyl carbamate derivative having a certain structure has not only excellent fungicidal activity but also extremely excellent systemicity in plants. The present invention is based on such finding.

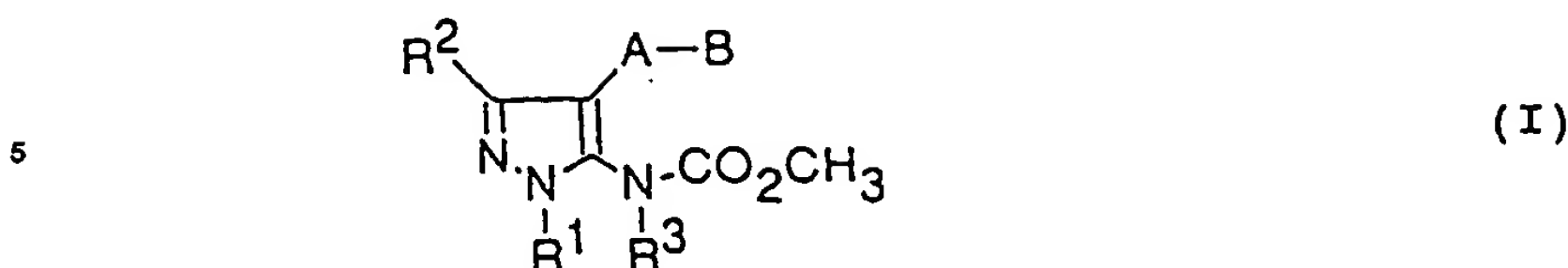
Thus, one object of the present invention is to provide a N-pyrazolyl carbamate derivative which has an excellent fungicidal activity.

Another object of the present invention is to provide an agricultural/horticultural fungicide containing the N-pyrazolyl carbamate derivative as an active ingredient, which has excellent preventive effects on various phytopathogenic fungi.

These objects as well as other objects and advantages of the present invention will become apparent to those skilled in the art from the following description.

SUMMARY OF THE INVENTION

The present invention provides a N-pyrazolyl carbamate derivative represented by the general formula (I):



10 wherein R¹ and R² independently indicate a hydrogen atom or a C₁-C₄ alkyl group; R³ is a hydrogen atom, a C₁-C₄ alkyl group, a C₂-C₅ alkynyl group, a C₂-C₄ alkylthioalkyl group or a C₂-C₄ alkoxyalkyl group; A is -O-, -C(O)-, -OCH₂-, -CH₂O-, -CH₂S-, -C≡C-, -CH=CH-, -CH₂CH₂-, -CH₂ON=C(R⁴)- or -CH=NOC(R⁴)(R⁵)- (wherein R⁴ and R⁵ independently indicate a hydrogen atom or a C₁-C₄ alkyl group); and B is a hydrogen atom, an optionally substituted aryl group or an optionally substituted heterocyclic group.

15 The present invention also provides an agricultural/horticultural fungicide containing the same as an active ingredient.

DETAILED DESCRIPTION OF THE INVENTION

20 The present invention will be explained in detail below.

The N-pyrazolyl carbamate derivative of the present invention is represented by the above formula (I). In the above formula (I), R¹ and R² independently indicate a hydrogen atom; or a C₁-C₄ alkyl group such as methyl group, ethyl group, n-propyl group, iso-propyl group, n-butyl group, sec-butyl group, etc. They indicate preferably hydrogen atom, methyl group or ethyl group, and more preferably, methyl group.

25 R³ is a hydrogen atom; a C₁-C₄ alkyl group such as methyl group, ethyl group, n-propyl group, iso-propyl group, n-butyl group, sec-butyl group, etc.; a C₂-C₅ alkynyl group such as ethynyl group, propargyl group, butynyl group, pentynyl group, etc.; a C₂-C₄ alkylthioalkyl group such as methylthiomethyl group, ethylthiomethyl group, etc.; or a C₂-C₄ alkoxyalkyl group such as methoxymethyl group, ethoxymethyl group, methoxyethyl group, ethoxyethyl group, etc. It is preferably hydrogen atom, C₂-C₅ alkynyl group or C₂-C₄ alkoxyalkyl group.

30 A is -O-, -C(O)-, -OCH₂-, -CH₂O-, -CH₂S-, -C≡C-, -CH=CH-, -CH₂CH₂-, -CH₂ON=C(R⁴)- or -CH=NOC(R⁴)(R⁵)-. It is preferably -O-, -OCH₂-, -CH₂O-, -CH₂S-, -C≡C-, -CH=CH-, -CH₂ON=C(R⁴)- or -CH=NOC(R⁴)(R⁵)-, and more preferably, -OCH₂-, -CH₂O-, -CH₂S-, -C≡C-, -CH₂ON=C(R⁴)- or -CH=NOC(R⁴)(R⁵)-. R⁴ and R⁵ independently indicate a hydrogen atom; or a C₁-C₄ alkyl group such as methyl group, ethyl group, n-propyl group, iso-propyl group, n-butyl group, sec-butyl group, etc. They indicate preferably hydrogen atom or C₁-C₂ alkyl group. More preferably, R⁴ is a hydrogen or a methyl group and R⁵ is a hydrogen atom.

35 B is a hydrogen atom; an optionally substituted aryl group such as phenyl group, naphthyl group, etc.; or an optionally substituted heterocyclic group such as pyridyl group, pirimidyl group, furanyl group, benzothiazolyl group, etc. It is preferably optionally substituted phenyl group, naphthyl group or pyridyl group, and more preferably, optionally substituted phenyl group.

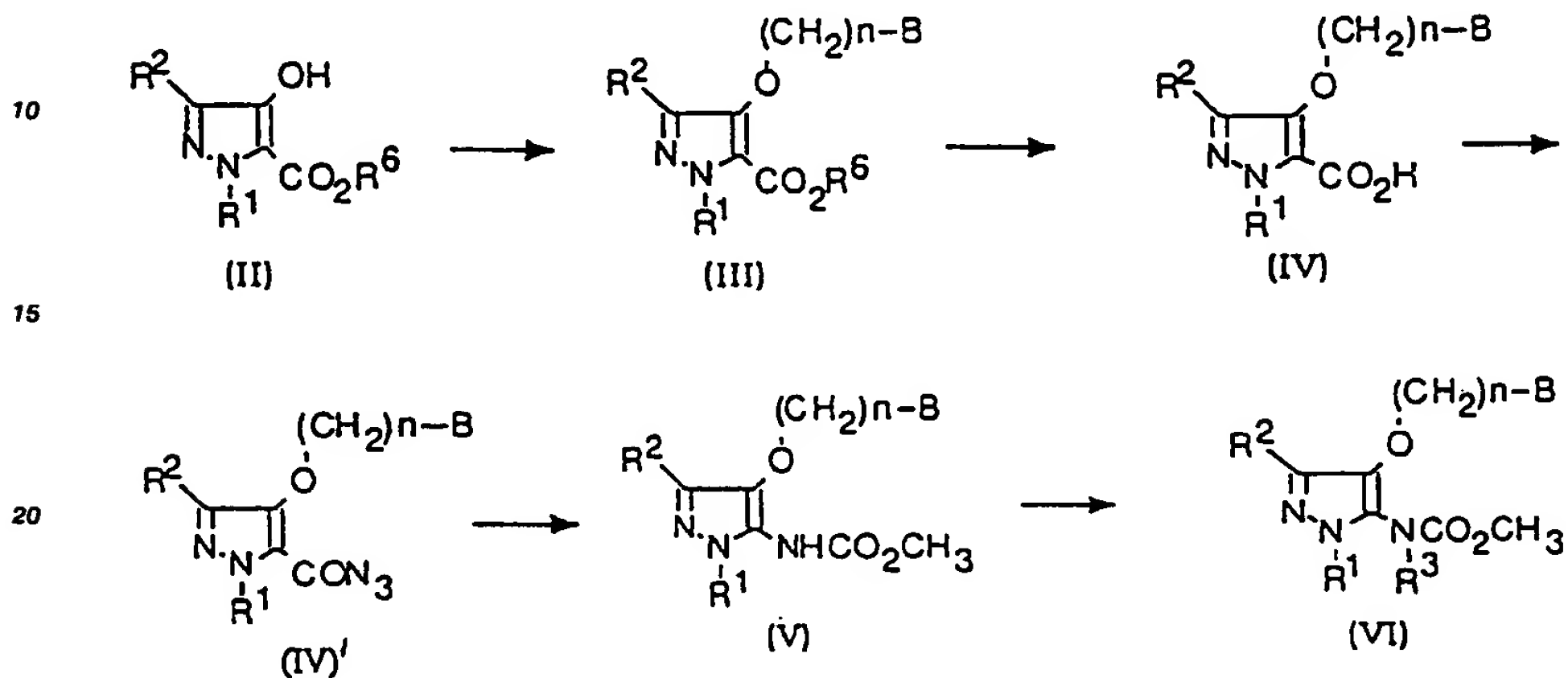
40 The aryl group and heterocyclic group may be substituted with a substituent selected from a group consisting of the following substituents: a cyano group; a nitro group; a halogen atom such as fluorine atom, chlorine atom, bromine atom, etc.; a C₁-C₄ alkyl group such as methyl group, ethyl group, n-propyl group, iso-propyl group, n-butyl group, sec-butyl group, etc.; a C₁-C₄ haloalkyl group such as trifluoromethyl group, difluoromethyl group, trichloromethyl group, dichlorodifluoroethyl group etc.; a C₁-C₆ alkoxy group such as methoxy group, ethoxy group, iso-propoxy group, n-butoxy group, etc. which may be substituted with a halogen atom or a C₃-C₆ cycloalkyl group; a C₁-C₆ alkylthio group such as methylthio group, ethylthio group, iso-propylthio group, n-butylthio group, etc.; a C₂-C₆ alkenyloxy group such as propenyloxy group, etc. which may be substituted with a halogen atom; a C₂-C₆ alkynyloxy group such as propargyloxy group, etc.; and a phenoxy group, a benzyloxy group, or a pyridyloxy group which may be substituted by the just mentioned cyano group, nitro group, halogen atom, C₁-C₄ alkyl group, C₁-C₄ haloalkyl group, C₁-C₆ alkoxy group, C₁-C₆ alkylthio group, C₁-C₆ alkenyloxy group, or C₁-C₆ alkynyloxy group.

50 Further, adjacent two substituents may bond together with an aryl group or a heterocyclic group to form a fused ring. The number of the substituent is 0 to 5, preferably 0 to 3. When containing a plurality of substituents, the substituents may be the same or different. Preferable examples of the substituent include halogen atom, C₁-C₄ alkyl group, C₁-C₄ haloalkyl group, C₁-C₆ alkoxy group which may be substituted with a halogen atom, phenoxy group and the like. More preferable examples of the substituent include halogen

atom; C₁-C₄ alkyl group; C₁-C₄ alkoxy group which may be substituted with a halogen atom, preferably with a fluorine atom; trifluoromethyl group; phenoxy group and the like.

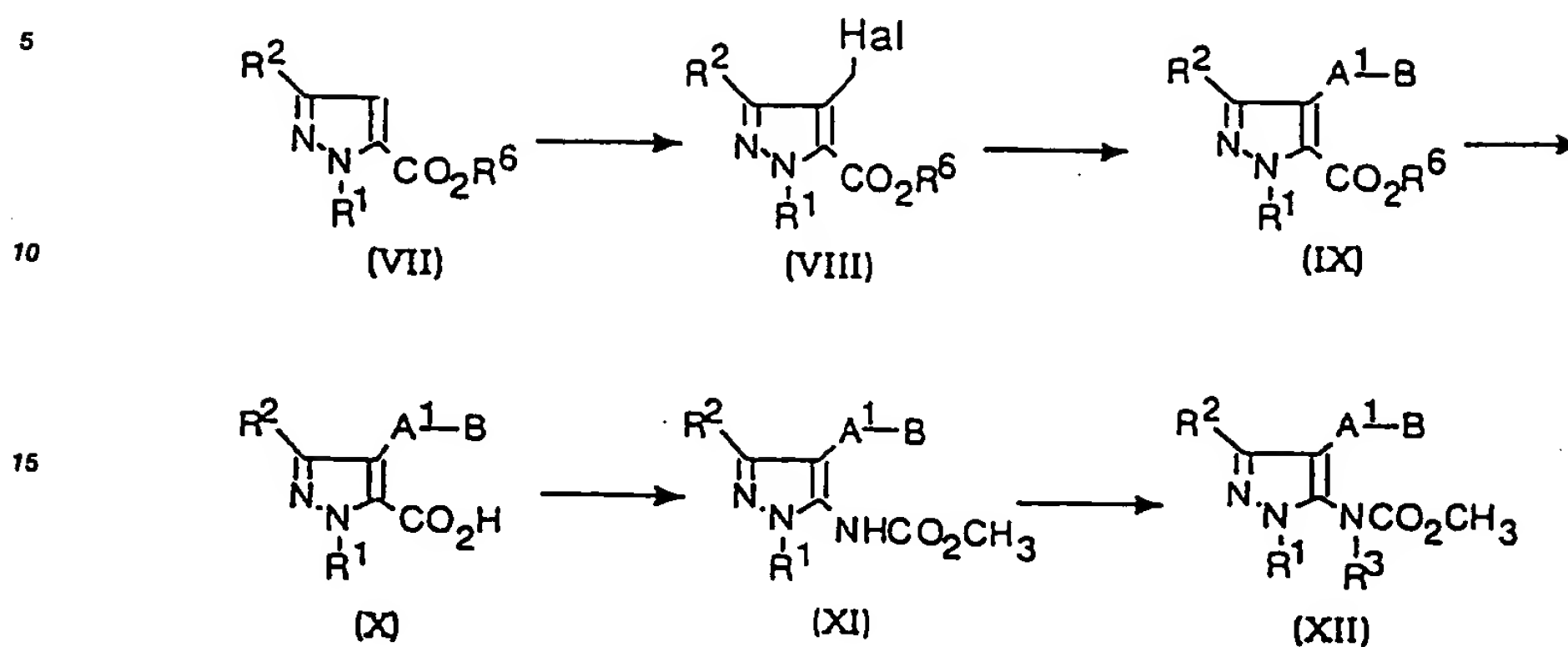
All compounds of the present invention are novel and they can be produced according to the following reaction scheme 1, 2 or 3.

(Reaction scheme 1)

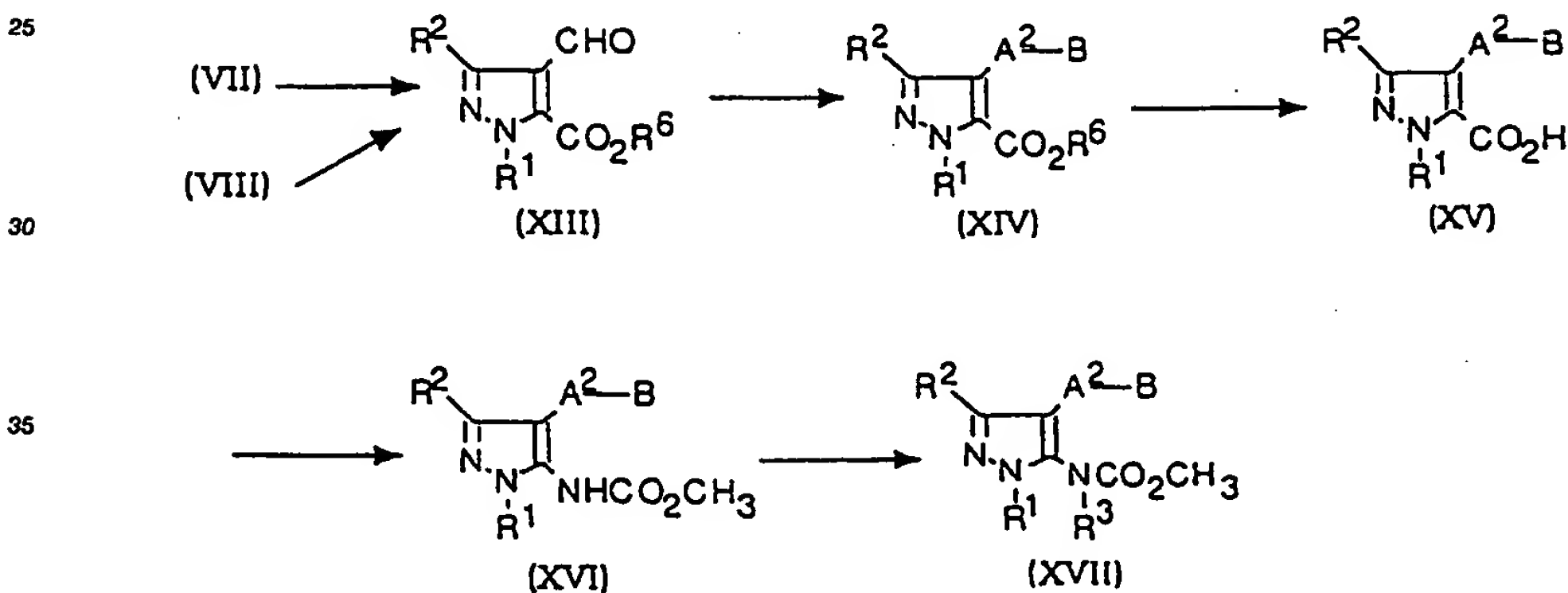


In the above reaction scheme, R¹, R², R³ and B are as defined in the above general formula (I); R⁶ is a C₁-C₄ alkyl group; and n is 0 or 1.

(Reaction scheme 2)



(Reaction scheme 3)



In the reaction schemes 2 and 3, R^1 , R^2 , R^3 and B are as defined in the above general formula (I); Hal is a chlorine atom or a bromine atom; R^6 is a C_1 - C_4 alkyl group; A^1 is $-CH_2O-$, $-CH_2S-$ or $-CH_2ON=C(R^4)-$ and A^2 is $-CH=NOC(R^4)(R^5)-$.

45 The above reaction scheme 1 shows a method comprising reacting a 4-hydroxy-5-alkoxycarbonyl pyrazole derivative (II) with a halide $-(CH_2)_nB$ in the presence of a base to give a corresponding ether derivative (III); converting a carboxylic acid derivative (IV), obtained by hydrolyzing an ester group with a suitable base, into a carboxylic acid halide with a halogenating agent; and then subjecting an azide derivative (IV)', obtained by treating sodium azide, to the Curtius rearrangement reaction in methanol to give a carbamate derivative (V). The carbamate derivative (V) can be reacted with a corresponding halide in the presence of a base to give a compound (IV). Further, 4-hydroxy-5-alkoxycarbonyl pyrazole (II) as a starting material can be produced by a method described in Japanese Patent Application No. 4-217668 or a similar method.

55 Examples of the base used in the reaction from (II) to (III) and the reaction from (V) to (VI) include alkali metal hydrides such as sodium hydride, etc.; alkali metal alcoholates such as sodium methylate, etc.; alkali metal carbonates such as potassium carbonate, etc.; alkali metal hydroxides such as potassium hydroxide, etc. Preferable examples include alkali metal hydrides and alkali metal carbonates.

Examples of the base used in the reaction from (III) to (IV) include alkali metal hydroxides such as sodium hydroxide, potassium hydroxide, etc.

Examples of the halogenating agent used in the reaction from (IV) to carboxylic acid halide include thionyl chloride, phosgene or phosphorous oxychloride. In this reaction, there can be used tertiary amines
 5 such as N-methylmorpholine, triethylamine, etc., aromatic bases such as pyridine, picoline, etc. in an inert solvent. The following solvent may be used alone in the azidation reaction, or the reaction may be carried out in two kinds of solvents in the presence or absence of a normal phase transfer catalyst.

Examples of the solvent used in these reactions include water; alcohols such as methanol, ethanol, etc.; ethers such as diethyl ether, tetrahydrofuran, etc.; polar solvents such as dimethylformamide, dimethyl
 10 sulfoxide, etc.; aromatic hydrocarbons such as toluene, chlorobenzene, etc.; alkyl halides such as methylene chloride, dichloroethane, etc.

The reaction scheme 2 shows a method comprising subjecting a 5-alkoxycarbonyl pyrazole derivative (VII) to chloromethylation or bromomethylation, converting into an ether, thioether or iminoxy derivative (IX) and then preparing carbamate derivatives (XI) and (XII) according to the same manner as that described in
 15 the reaction scheme 1.

The chloromethylation or bromomethylation reaction from (VII) to (VIII) can be carried out according to a method described in Org. Synth., III, 195 or a similar method. The derivative (VIII) can be reacted with B-OH, B-SH or an oxime derivative in an inert solvent {e.g., alcohols such as methanol, ethanol, etc.; ethers such as diethyl ether, tetrahydrofuran, etc.; polar solvents such as dimethylformamide (DMF), dimethyl
 20 sulfoxide, etc.; aromatic hydrocarbons such as toluene, chlorobenzene, etc.} in the presence of a suitable base (e.g., alkali metal hydrides such as sodium hydride, etc.; alkali metal alcoholates such as sodium methylate, etc.; alkali metal carbonates such as potassium carbonate, etc.; alkali metal hydroxides such as potassium hydroxide, etc.) to give an ether, thioether or iminoxy derivative (IX).

The reaction scheme 3 shows a method comprising subjecting a 5-alkoxycarbonyl pyrazole derivative (VII) to the Vilsmeier reaction or subjecting a chloromethyl or bromomethyl derivative (VIII) to the oxidation
 25 reaction to give an aldehyde derivative (XIII) and, after subjecting to imination, preparing carbamate derivatives (XVI) and (XVII).

The Vilsmeier reaction of the compound (VII) itself is a known method and can be carried out according to a method described in Org. Synth., III, 98 (1955) or Zh. Org. Khim., 9, 815 (1973) or a similar
 30 method. The oxidation reaction of the compound (VIII) can be carried out by a method of treating N-oxide of tertiary amine (e.g., N-methylmorpholine or triethylamine) in an inert solvent (e.g., methylene chloride or acetonitrile).

The resulting aldehyde derivative (XIII) can be reacted with a corresponding oxyamine derivative in an inert solvent (e.g., alcohols such as methanol, ethanol, etc.; ethers such as diethyl ether, tetrahydrofuran,
 35 etc.; polar solvents such as dimethylformamide, dimethyl sulfoxide, etc.; aromatic hydrocarbons such as toluene, chlorobenzene, etc.) to give an imino derivative (XIV).

All reactions described in reaction schemes 1 to 3 are carried out at a temperature within a range from -20°C to the boiling point of the solvent to be used.

The compounds of the present invention thus obtained are each novel one having an excellent
 40 fungicidal activity. They exert excellent preventive effects on various phytopathogenic fungi, which makes them useful as an agricultural/horticultural fungicide.

For example, the compound of the present invention has a high activity against rice blast (*Pyricularia oryzae*), rice sheath blight (*Rhizoctonia solani*), wheats powdery mildew (*Erysiphe graminis* f. sp. *tritici*),
 45 barley powdery mildew (*E. graminis* f. sp. *hedei*), various leaf rusts of wheat and barley (e.g., *Puccinia recondita*), gray mold of vegetables and fruit trees (*Botrytis cinerea*), late blight of various crops (*Phytophthora infestans*) and the like. Further, they have prolonged residual activity and excellent systemicity in plants, which makes them highly useful as an agricultural/horticultural fungicide.

When using the compound of the present invention as an agricultural/horticultural fungicide, the compound may be used as it is. It is preferable to formulate said compound into, for example, emulsifiable
 50 concentrates, wettable powders, dust or granules by blending with adjuvants in a conventional manner to thereby ensure the effective dispersion of the active ingredient at the application.

When using the agricultural/horticultural fungicide of the present invention in the form of emulsifiable concentrate, a raw material obtained by mixing 10 to 80 parts (preferably 10 to 70 parts) of the compound of the present invention, 10 to 90 parts (preferably 20 to 80 parts) of a solvent and 3 to 20 parts (preferably
 55 5 to 15 parts) of a surfactant is diluted with water to a predetermined concentration and the resulting chemical solution is applied by a method such as spraying.

When using the fungicide in the form of wettable powder, a raw material obtained by mixing 5 to 80 parts (preferably 10 to 70 parts) of the compound of the present invention, 10 to 90 parts (preferably 20 to

80 parts) of an extender and 1 to 20 parts (preferably 3 to 15 parts) of a surfactant is diluted with water to a predetermined concentration according to the same manner as the case of emulsifiable concentrate.

When using the fungicide in the form of dust, a raw material obtained by mixing 0.1 to 10 parts (preferably 1 to 5 parts) of the compound of the present invention and 90 to 99.9 parts (preferably 95 to 99 parts) of an extender such as kaolin, bentonite, talc, etc. is used as it is.

The agricultural/horticultural fungicide of the present invention can also be used after mixing with other active ingredients which do not inhibit the fungicidal effect of the active ingredient of the present invention such as fungicides, insecticides, acaricides and the like.

The agricultural/horticultural fungicide of the present invention can be suitably applied for both foliar application and submerged application. In case of foliar application, emulsifiable concentrates or wettable powders are normally diluted with water to the concentration (concentration of active ingredient) of 10 to 1000 ppm and the resulting solution may be applied in an amount of 10 to 500 liters per 10 ares.

Among the compounds represented by the above formulas (VIII) and (XIII), a compound wherein R¹ and R² indicate an C₁-C₄ alkyl group is novel and is useful as a production intermediate of the compound of the general formula (I).

As described above, all compounds of the present invention are novel compounds and they have an excellent fungicidal activity. Since the compound of the present invention has an excellent control effect on various phytopathogenic fungi, it is useful as an agricultural/horticultural fungicide.

20 Examples

The following Examples further illustrate the present invention in detail but are not to be construed as to limiting the scope thereof.

25 Example 1

Synthesis of methyl N-{1,3-dimethyl-4-(2,5-dimethylbenzyloxy)pyrazole-5-yl}-N-propargyl-carbamate (compound No. 50 in Table 1)

30 A DMF solution (10 ml) of methyl 1,3-dimethyl-4-hydroxypyrazole-5-ylcarboxylate (1 g), 2,5-dimethylbenzyl chloride (0.95 g) and K₂CO₃ (0.98 g) were heated with stirring for 2 hours. 30 ml of ethyl acetate was added, and the mixture was washed in turn with water and brine and then dried over anhydrous sodium sulfate. The solvent was distilled off to give a crude benzyl ether derivative (1.5 g).

An aqueous NaOH solution (NaOH: 0.25 g, H₂O: 5 ml) was added to an ethanol (5 ml) solution of the benzyl ether derivative (1.5 g) and the mixture was heated under reflux condition for two hours. After cooling, it was neutralized by adding concentrated HCl (0.65 ml), followed by extracting with 30 ml of ethyl acetate. Then, the organic layer was washed in turn with water and brine and dried over anhydrous sodium sulfate. The solvent was distilled off and the resulting residue was recrystallized from a mixed solvent of ethyl acetate/hexane to give a carboxylic acid derivative (1.4 g).

40 To 15 ml of a methylene chloride solution of the carboxylic acid derivative (1.4 g), pyridine (0.7 g) and thionyl chloride (0.77 g) were added in turn under water cooling. After stirring for 2 hours, an aqueous sodium azide solution (NaN₃: 0.5 g, H₂O: 2 ml) and (n-C₄H₉)₄NCl (0.05 g) were added. After stirring for 3 hours, 30 ml of methylene chloride was added, and the organic layer was washed in turn with water and brine and then dried over anhydrous sodium sulfate. The solvent was distilled off to give a crude azide derivative (1.5 g).

To the crude azide derivative (1.5 g), 20 ml of methanol was added and the mixture was heated under reflux condition for 4 hours. After the solvent was distilled off, the residue was chromatographed (SiO₂: 50 g, hexane/ethyl acetate = 1/1) to give a 1.3 g of methyl N-{1,3-dimethyl-4-(2,5-dimethylbenzyloxy)pyrazole-5-yl} carbamate (compound No. 48 in Table 1).

50 To 5 ml of a DMF solution of the carbamate derivative (0.8 g, compound No. 48 in Table 1), 60% NaH (0.11 g) was added and the mixture was stirred for 20 minutes. Then, propargyl bromide (1 g) was added, followed by stirring for one hour. After 30 ml of ethyl acetate was added, the mixture was washed in turn with water and brine and dried over anhydrous sodium sulfate. The solvent was distilled off, and then the residue was chromatographed (SiO₂: 50 g, hexane/ethyl acetate = 1/1) to give 0.8 g of a titled compound.

55

Example 2

Synthesis of methyl N-[1,3-dimethyl-4- $\{(\alpha\text{-methyl-4-trifluoromethyl-benzylidene)aminooxymethyl pyrazole-5-yl}\}$]-N-propargyl-carbamate (compound No. 169 in Table 1)

5

To a solution of ethyl 1,3-dimethylpyrazole-5-ylcarboxylate (16.3 g), phosphoric acid (11 ml), concentrated hydrochloric (27 ml) and acetic acid (50 ml), paraformaldehyde (6 g) was added and the mixture was heated at 100 °C with stirring for 5 hours. After cooling, the reaction mixture was poured into ice and neutralized with Na₂CO₃, and extracted with 200 ml of ethyl acetate. The extract was washed in turn with
10 water and brine and dried over anhydrous sodium sulfate. The solvent was distilled off and the residue was chromatographed (SiO₂: 150 g, hexane/ethyl acetate = 4/1) to give 8 g of ethyl 4-chloromethyl-1,3-dimethylpyrazole-5-ylcarboxylate.

¹H-NMR (CDCl₃); 1.42 (3H, t), 2.30 (3H, s), 4.12 (3H, s), 4.42 (2H, q), 4.75 (2H, s)

60% NaH (0.2 g) was added to a DMF solution (5 ml) of 4-trifluoromethylacetophenone oxime (1 g) and
15 the mixture was stirred for 20 minutes. Then, ethyl 4-chloromethyl-1,3-dimethylpyrazole-5-ylcarboxylate (1 g) was added and the mixture was stirred and allowed to stand overnight. After 30 ml of ethyl acetate was added, the organic layer was washed in turn with water and brine and then dried over anhydrous sodium sulfate. The solvent was distilled off to give a crude oxime ether derivative (1.8 g).

To 10 ml of an ethanol solution of the oxime ether derivative (1.8 g), an aqueous NaOH solution (NaOH:
20 0.24 g, H₂O: 5 ml) was added and the mixture was heated under reflux condition for 2 hours. After cooling, the reaction mixture was neutralized by adding concentrated HCl (0.6 ml). After 30 ml of ethyl acetate was added, the organic layer was washed in turn with water and saturated saline and then dried over anhydrous sodium sulfate. The solvent was distilled off and the resulting residue was recrystallized from a mixed solvent of ethyl acetate/hexane to give a carboxylic acid derivative (1.6 g).

25 To 15 ml of a methylene chloride solution of the carboxylic acid derivative (1.6 g), pyridine (0.6 g) and thionyl chloride (0.6 g) were added in turn under water cooling. After stirring for 2 hours, an aqueous sodium azide solution (NaN₃: 0.4 g, H₂O: 2 ml) and (n-C₄H₉)₄NCl (0.05 g) were added. After stirring for 3 hours, 30 ml of methylene chloride was added, and the organic layer was washed in turn with water and brine and then dried over anhydrous sodium sulfate. The solvent was distilled off to give a crude azide
30 derivative (1.6 g).

To the crude azide derivative (1.6 g), 20 ml of methanol was added and the mixture was heated under reflux condition for 4 hours. After the solvent was distilled off, the residue was chromatographed (SiO₂: 50 g, hexane/ethyl acetate = 1/1) to give a 1.4 g of methyl N-[1,3-dimethyl-4- $\{(\alpha\text{-methyl-4-trifluoromethylbenzylidene)aminooxymethyl pyrazole-5-yl}\}$] carbamate (compound No. 167 in Table 1).

35 To 5 ml of a DMF solution of the carbamate derivative (1.4 g, compound No. 167 in Table 1), 60% NaH (0.16 g) was added and the mixture was stirred for 20 minutes. Then, propargyl bromide (1 g) was added and the mixture was stirred for one hour. After 30 ml of ethyl acetate was added, the mixture was washed in turn with water and brine and then dried over anhydrous sodium sulfate. After the solvent was distilled off, the residue was chromatographed (SiO₂: 50 g, hexane/ethyl acetate = 1/1) to give 1.2 g of a titled
40 compound.

Example 3

45 Synthesis of N-{1,3-dimethyl-4- $\{(\alpha\text{-methyl-3-trifluoromethyl-benzylideneoxyiminomethyl)pyrazole-5-yl}\}$ carbamate (compound No. 194 in Table 1)

To a mixture of ethyl 1,3-dimethylpyrazole-5-ylcarboxylate (20.0 g) and a 30% hydrogen bromide-acetic acid solution (60 ml), paraformaldehyde (7.2 g) was added and the mixture was stirred at 80 - 90 °C for 2 hours and a half. The reaction mixture was poured into ice water and the solution was neutralized with
50 sodium acetate trihydrate (41 g). After extracting with ethyl acetate, the extract was washed in turn with an aqueous saturated sodium bicarbonate solution and brine and then dried over anhydrous sodium sulfate. After the solvent was distilled off, the residue was chromatographed (SiO₂: 200 g, hexane/ethyl acetate = 4/1) to give 26.8 g of ethyl 4-bromomethyl-1,3-dimethylpyrazole-5-ylcarboxylate (yield: 86.3%).

¹H-NMR (CDCl₃); 1.45 (3H, t), 2.28 (3H, s), 4.09 (3H, s), 4.42 (2H, q), 4.65 (2H, s),

55 ¹³C-NMR (CDCl₃); 11.3, 14.1, 23.2, 39.8, 61.4, 120.3, 130.3, 147.1, 159.7

To 20 ml of an acetonitrile solution of ethyl 4-bromomethyl-1,3-dimethylpyrazole-5-ylcarboxylate (2.9 g, 11.1 mmol) and molecular sieves 4A (3 g), N-methylmorpholine-N-oxid (2.6 g, 22.2 mmol) was added under water cooling, followed by stirring at room temperature for 48 hours. The mixed solution was filtered

with celite and the filtrate was concentrated. To the resulting residue, ethyl acetate was added and the mixture was washed in turn with water and brine and then dried over anhydrous sodium sulfate. After the solvent was distilled off, the resulting residue was recrystallized from hexane/ethyl acetate to give 1.7 g of ethyl 1,3-dimethyl-4-formylpyrazole-5-ylcarboxylate (yield: 78%).

5 ¹H-NMR (CDCl₃); 1.44 (3H, t), 2.49 (3H, s), 4.14 (3H, s), 4.47 (2H, q), 10.39 (1H, s)

To 15 ml of an ethanol solution of ethyl 1,3-dimethyl-4-formylpyrazole-5-ylcarboxylate (1.5 g, 7.65 mmol), α-methyl-3-trifluoromethylbenzyloxyamine (1.6 g, 7.80 mmol) was added and the mixture was stirred at room temperature for 12 hours. The reaction solution was concentrated and the residue was chromatographed (SiO₂: 40 g, hexane/ethyl acetate = 4/1) to give 2.5 g of ethyl {1,3-dimethyl-4-(α-methyl-3-trifluoromethyl-benzyloxyiminomethyl)pyrazole-5-yl} carboxylate (yield: 85.3%).

10 ¹H-NMR (CDCl₃); 1.42 (3H, t), 1.63 (3H, d), 2.23 (3H, s), 4.07 (3H, s), 4.40 (2H, q), 4.73 (1H, q), 7.4-7.65 (4H, m), 8.56 (1H, s)

According to the same manner as that described in Examples 1 and 2, the resulting ethyl carboxylate derivative (2.5 g) was subjected in turn to hydrolysis, azidation and Curtius rearrangement reactions to give the titled compound (1.9 g).

15 According to the same manner as that described above except for an alteration in the starting material, a compound in Table 1 can be synthesized.

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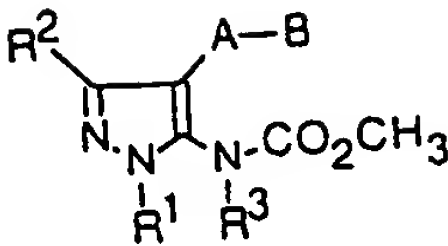
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Table 1



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Compound No.	R1	R2	R3	A	B	Physical properties
1	CH3	CH3	H	O	H	White crystal
2	CH3	CH3	H	O	5-CF3-pyridin-2-yl	White crystal
3	CH3	CH3	CH2OCH3	O	5-CF3-pyridin-2-yl	Viscous liquid
4	CH3	CH3	propargyl	O	5-CF3-pyridin-2-yl	Viscous liquid
5	CH3	CH3	CH2SCH3	O	5-CF3-pyridin-2-yl	Viscous liquid
6	CH3	CH3	CH2OCH3	O	4-CF3-pyridin-2-yl	Viscous liquid
7	CH3	CH3	propargyl	O	4-CF3-pyridin-2-yl	Viscous liquid
8	CH3	CH3	CH2OCH3	O	3-CF3-pyridin-2-yl	Viscous liquid
9	CH3	CH3	propargyl	O	3-CF3-pyridin-2-yl	Viscous liquid
10	CH3	CH3	CH2OCH3	O	4-CF3-6-Cl-pyridin-2-yl	Viscous liquid
11	CH3	CH3	propargyl	O	4-CF3-6-Cl-pyridin-2-yl	Viscous liquid
12	CH3	CH3	CH2OCH3	O	4-Cl-pyridin-2-yl	Viscous liquid
13	CH3	CH3	C2H5	O	4-Cl-pyridin-2-yl	Viscous liquid
14	CH3	CH3	propargyl	O	4,6-Cl2-pyridin-2-yl	Viscous liquid
15	CH3	CH3	propargyl	O	5-Cl-2-NO2-phenyl	Viscous liquid
16	CH3	CH3	C2H5	O	3-Cl-phenyl	Viscous liquid
17	CH3	CH3	propargyl	O	3-PhO-phenyl	Viscous liquid
18	CH3	CH3	propargyl	O	3-Cl-4-NO2-phenyl	Viscous liquid
19	CH3	CH3	propargyl	O	6-(2'-CN-PhO)pyrimidin-4-yl	Viscous liquid
20	CH3	CH3	propargyl	O	4-(2'-CN-PhO)pyrimidin-2-yl	Viscous liquid
21	CH3	CH3	H	OCH2	Phenyl	White crystal
22	CH3	CH3	CH2OCH3	OCH2	Phenyl	Viscous liquid
23	CH3	CH3	propargyl	OCH2	Phenyl	Viscous liquid
24	CH3	CH3	CH2SCH3	OCH2	Phenyl	Viscous liquid
25	CH3	CH3	H	OCH2	3-Cl-phenyl	White crystal

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Table 1 (Continued)

		<i>R</i> ₁	<i>R</i> ₂	<i>A</i>	<i>B</i>		
5	26	CH ₃	CH ₃	C ₂ H ₅	OCH ₂	3-Cl-phenyl	Viscous liquid
	27	CH ₃	CH ₃	CH ₂ OCH ₃	OCH ₂	3-Cl-phenyl	Viscous liquid
	28	CH ₃	CH ₃	CH ₂ SCH ₃	OCH ₂	3-Cl-phenyl	Viscous liquid
10	29	CH ₃	CH ₃	propargyl	OCH ₂	3-Cl-phenyl	Viscous liquid
	30	CH ₃	CH ₃	propargyl	OCH ₂	2-Cl-phenyl	Viscous liquid
	31	CH ₃	CH ₃	CH ₂ OCH ₃	OCH ₂	2-Cl-phenyl	Viscous liquid
15	32	CH ₃	CH ₃	propargyl	OCH ₂	4-Cl-phenyl	Viscous liquid
	33	CH ₃	CH ₃	CH ₂ OCH ₃	OCH ₂	4-Cl-phenyl	Viscous liquid
	34	CH ₃	CH ₃	propargyl	OCH ₂	2,4-Cl ₂ -phenyl	Viscous liquid
20	35	CH ₃	CH ₃	CH ₂ OCH ₃	OCH ₂	2,4-Cl ₂ -phenyl	Viscous liquid
	36	CH ₃	CH ₃	H	OCH ₂	2,5-Cl ₂ -phenyl	White crystal
	37	CH ₃	CH ₃	C ₂ H ₅	OCH ₂	2,5-Cl ₂ -phenyl	Viscous liquid
	38	CH ₃	CH ₃	CH ₂ OCH ₃	OCH ₂	2,5-Cl ₂ -phenyl	Viscous liquid
25	39	CH ₃	CH ₃	CH ₂ SCH ₃	OCH ₂	2,5-Cl ₂ -phenyl	Viscous liquid
	40	CH ₃	CH ₃	propargyl	OCH ₂	2,5-Cl ₂ -phenyl	Viscous liquid
	41	CH ₃	CH ₃	CH ₂ OCH ₃	OCH ₂	2-Me-phenyl	Viscous liquid
30	42	CH ₃	CH ₃	propargyl	OCH ₂	2-Me-phenyl	Viscous liquid
	43	CH ₃	CH ₃	CH ₂ OCH ₃	OCH ₂	3-Me-phenyl	Viscous liquid
	44	CH ₃	CH ₃	propargyl	OCH ₂	3-Me-phenyl	Viscous liquid
35	45	CH ₃	CH ₃	propargyl	OCH ₂	4-Me-phenyl	Viscous liquid
	46	CH ₃	CH ₃	propargyl	OCH ₂	2,4-Me ₂ -phenyl	Viscous liquid
	47	CH ₃	CH ₃	CH ₂ OCH ₃	OCH ₂	2,4-Me ₂ -phenyl	Viscous liquid
40	48	CH ₃	CH ₃	H	OCH ₂	2,5-Me ₂ -phenyl	White crystal
	49	CH ₃	CH ₃	CH ₂ OCH ₃	OCH ₂	2,5-Me ₂ -phenyl	Viscous liquid
	50	CH ₃	CH ₃	propargyl	OCH ₂	2,5-Me ₂ -phenyl	Viscous liquid
45	51	CH ₃	CH ₃	CH ₂ OCH ₃	OCH ₂	2-Me-5-Cl-phenyl	Viscous liquid
	52	CH ₃	CH ₃	propargyl	OCH ₂	2-Me-5-Cl-phenyl	Viscous liquid
	53	CH ₃	CH ₃	CH ₂ OCH ₃	OCH ₂	2-Me-5-SMe-phenyl	Viscous liquid
50	54	CH ₃	CH ₃	propargyl	OCH ₂	2-CHF ₂ O-phenyl	Viscous liquid
	55	CH ₃	CH ₃	CH ₂ OCH ₃	OCH ₂	2-CHF ₂ O-phenyl	Viscous liquid

Table 1 (Continued)

5	56	CH ₃	CH ₃	propargyl	OCH ₂	3-CHF ₂ O-phenyl	Viscous liquid
	57	CH ₃	CH ₃	CH ₂ OCH ₃	OCH ₂	3-CHF ₂ O-phenyl	Viscous liquid
	58	CH ₃	CH ₃	propargyl	OCH ₂	4-CHF ₂ O-phenyl	Viscous liquid
	59	CH ₃	CH ₃	CH ₂ OCH ₃	OCH ₂	4-CHF ₂ O-phenyl	Viscous liquid
10	60	CH ₃	CH ₃	propargyl	OCH ₂	2-Me-4-CHF ₂ O-phenyl	Viscous liquid
	61	CH ₃	CH ₃	CH ₂ OCH ₃	OCH ₂	2-Me-5-CHF ₂ O-phenyl	Viscous liquid
	62	CH ₃	CH ₃	H	OCH ₂	2-Cl-4-CHF ₂ O-phenyl	White crystal
15	63	CH ₃	CH ₃	CH ₂ OCH ₃	OCH ₂	2-Cl-4-CHF ₂ O-phenyl	Viscous liquid
	64	CH ₃	CH ₃	propargyl	OCH ₂	2-Cl-4-CHF ₂ O-phenyl	Viscous liquid
	65	CH ₃	CH ₃	H	OCH ₂	2-Cl-5-CHF ₂ O-phenyl	Viscous liquid
20	66	CH ₃	CH ₃	CH ₂ OCH ₃	OCH ₂	2-Cl-5-CHF ₂ O-phenyl	Viscous liquid
	67	CH ₃	CH ₃	propargyl	OCH ₂	2-Cl-5-CHF ₂ O-phenyl	Viscous liquid
	68	CH ₃	CH ₃	H	OCH ₂	5-Cl-2-CHF ₂ O-phenyl	Viscous
25	69	CH ₃	CH ₃	CH ₂ OCH ₃	OCH ₂	5-Cl-2-CHF ₂ O-phenyl	Viscous liquid
	70	CH ₃	CH ₃	propargyl	OCH ₂	5-Cl-2-CHF ₂ O-phenyl	Viscous liquid
	71	CH ₃	CH ₃	H	OCH ₂	2,5-(CHF ₂ O) ₂ -phenyl	White crystal
30	72	CH ₃	CH ₃	CH ₂ OCH ₃	OCH ₂	2,5-(CHF ₂ O) ₂ -phenyl	Viscous liquid
	73	CH ₃	CH ₃	propargyl	OCH ₂	2,5-(CHF ₂ O) ₂ -phenyl	Viscous liquid
	74	CH ₃	CH ₃	propargyl	OCH ₂	2,4-(CHF ₂ O) ₂ -phenyl	Viscous liquid
35	75	CH ₃	CH ₃	C ₂ H ₅	OCH ₂	3-PhO-phenyl	Viscous liquid
	76	CH ₃	CH ₃	CH ₂ OCH ₃	OCH ₂	3-PhO-phenyl	Viscous liquid
	77	CH ₃	CH ₃	propargyl	OCH ₂	3-PhO-phenyl	Viscous liquid
40	78	CH ₃	CH ₃	propargyl	OCH ₂	2-CF ₃ -phenyl	Viscous liquid
	79	CH ₃	CH ₃	propargyl	OCH ₂	3-CF ₃ -phenyl	Viscous liquid
	80	CH ₃	CH ₃	propargyl	OCH ₂	4-CF ₃ -phenyl	Viscous liquid
45	81	CH ₃	CH ₃	CH ₂ OCH ₃	OCH ₂	2,5-(CF ₃) ₂ -phenyl	Viscous liquid
	82	CH ₃	CH ₃	propargyl	OCH ₂	2,5-(CF ₃) ₂ -phenyl	Viscous liquid
	83	CH ₃	CH ₃	CH ₂ OCH ₃	OCH ₂	3,5-(CF ₃) ₂ -phenyl	Viscous liquid
50	84	CH ₃	CH ₃	propargyl	OCH ₂	3,5-(CF ₃) ₂ -phenyl	Viscous liquid
	85	CH ₃	CH ₃	propargyl	OCH ₂	3-benzyloxy-phenyl	Viscous liquid

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Table 1 (Continued)

5	86	CH ₃	CH ₃	propargyl	OCH ₂	2-naphthyl	Viscous liquid
	87	CH ₃	CH ₃	CH ₂ OCH ₃	OCH ₂	2-naphthyl	Viscous liquid
	88	CH ₃	CH ₃	propargyl	OCH ₂	3-naphthyl	Viscous liquid
	89	CH ₃	CH ₃	CH ₂ OCH ₃	OCH ₂	3-naphthyl	Viscous liquid
10	90	CH ₃	CH ₃	propargyl	OCH ₂	2,2-Me ₂ -dihydrobenzofuran-5-yl	Viscous liquid
	91	CH ₃	CH ₃	H	CH ₂ O	Phenyl	White crystal
	92	CH ₃	CH ₃	CH ₂ OCH ₃	CH ₂ O	Phenyl	Viscous liquid
15	93	CH ₃	CH ₃	propargyl	CH ₂ O	Phenyl	Viscous liquid
	94	CH ₃	CH ₃	CH ₂ SCH ₃	CH ₂ O	Phenyl	Viscous liquid
	95	CH ₃	CH ₃	H	CH ₂ O	3-Cl-phenyl	White crystal
20	96	CH ₃	CH ₃	C ₂ H ₅	CH ₂ O	3-Cl-phenyl	Viscous liquid
	97	CH ₃	CH ₃	CH ₂ OCH ₃	CH ₂ O	3-Cl-phenyl	Viscous liquid
	98	CH ₃	CH ₃	CH ₂ SCH ₃	CH ₂ O	3-Cl-phenyl	Viscous liquid
25	99	CH ₃	CH ₃	propargyl	CH ₂ O	3-Cl-phenyl	Viscous liquid
	100	CH ₃	CH ₃	propargyl	CH ₂ O	2-Cl-phenyl	Viscous liquid
	101	CH ₃	CH ₃	CH ₂ OCH ₃	CH ₂ O	2-Cl-phenyl	Viscous liquid
30	102	CH ₃	CH ₃	propargyl	CH ₂ O	4-Cl-phenyl	Viscous liquid
	103	CH ₃	CH ₃	CH ₂ OCH ₃	CH ₂ O	4-Cl-phenyl	Viscous liquid
	104	CH ₃	CH ₃	propargyl	CH ₂ O	2,4-Cl ₂ -phenyl	Viscous liquid
35	105	CH ₃	CH ₃	CH ₂ OCH ₃	CH ₂ O	2,4-Cl ₂ -phenyl	Viscous liquid
	106	CH ₃	CH ₃	H	CH ₂ O	2,5-Cl ₂ -phenyl	White crystal
	107	CH ₃	CH ₃	C ₂ H ₅	CH ₂ O	2,5-Cl ₂ -phenyl	Viscous liquid
40	108	CH ₃	CH ₃	CH ₂ OCH ₃	CH ₂ O	2,5-Cl ₂ -phenyl	Viscous liquid
	109	CH ₃	CH ₃	CH ₂ SCH ₃	CH ₂ O	2,5-Cl ₂ -phenyl	Viscous liquid
	110	CH ₃	CH ₃	propargyl	CH ₂ O	2,5-Cl ₂ -phenyl	Viscous liquid
45	111	CH ₃	CH ₃	CH ₂ OCH ₃	CH ₂ O	2-Me-phenyl	Viscous liquid
	112	CH ₃	CH ₃	propargyl	CH ₂ O	2-Me-phenyl	Viscous liquid
	113	CH ₃	CH ₃	CH ₂ OCH ₃	CH ₂ O	3-Me-phenyl	Viscous liquid
	114	CH ₃	CH ₃	propargyl	CH ₂ O	3-Me-phenyl	Viscous liquid
50	115	CH ₃	CH ₃	propargyl	CH ₂ O	4-Me-phenyl	Viscous liquid

Table 1 (Continued)

5	116	CH ₃	CH ₃	H	CH ₂ O	2,4-Me ₂ -phenyl	Viscous liquid
	117	CH ₃	CH ₃	propargyl	CH ₂ O	2,4-Me ₂ -phenyl	Viscous liquid
	118	CH ₃	CH ₃	H	CH ₂ O	2,5-Me ₂ -phenyl	White crystal
10	119	CH ₃	CH ₃	CH ₂ OCH ₃	CH ₂ O	2,5-Me ₂ -phenyl	Viscous liquid
	120	CH ₃	CH ₃	propargyl	CH ₂ O	2,5-Me ₂ -phenyl	Viscous liquid
	121	CH ₃	CH ₃	CH ₂ OCH ₃	CH ₂ O	2-Me-5-Cl-phenyl	Viscous liquid
15	122	CH ₃	CH ₃	propargyl	CH ₂ O	2-Me-5-Cl-phenyl	Viscous liquid
	123	CH ₃	CH ₃	CH ₂ OCH ₃	CH ₂ O	2-Me-5-SMe-phenyl	Viscous liquid
	124	CH ₃	CH ₃	propargyl	CH ₂ O	2-CHF ₂ O-phenyl	Viscous liquid
20	125	CH ₃	CH ₃	CH ₂ OCH ₃	CH ₂ O	2-CHF ₂ O-phenyl	Viscous liquid
	126	CH ₃	CH ₃	propargyl	CH ₂ O	3-CHF ₂ O-phenyl	Viscous liquid
	127	CH ₃	CH ₃	CH ₂ OCH ₃	CH ₂ O	3-CHF ₂ O-phenyl	Viscous liquid
	128	CH ₃	CH ₃	propargyl	CH ₂ O	4-CHF ₂ O-phenyl	Viscous liquid
25	129	CH ₃	CH ₃	CH ₂ OCH ₃	CH ₂ O	4-CHF ₂ O-phenyl	Viscous liquid
	130	CH ₃	CH ₃	propargyl	CH ₂ O	2-Me-4-CHF ₂ O-phenyl	Viscous liquid
	131	CH ₃	CH ₃	CH ₂ OCH ₃	CH ₂ O	2-Me-5-CHF ₂ O-phenyl	Viscous liquid
30	132	CH ₃	CH ₃	H	CH ₂ O	2-Cl-4-CHF ₂ O-phenyl	White crystal
	133	CH ₃	CH ₃	CH ₂ OCH ₃	CH ₂ O	2-Cl-4-CHF ₂ O-phenyl	Viscous liquid
	134	CH ₃	CH ₃	propargyl	CH ₂ O	2-Cl-4-CHF ₂ O-phenyl	Viscous liquid
35	135	CH ₃	CH ₃	H	CH ₂ O	2-Cl-5-CHF ₂ O-phenyl	White crystal
	136	CH ₃	CH ₃	CH ₂ OCH ₃	CH ₂ O	2-Cl-5-CHF ₂ O-phenyl	Viscous liquid
	137	CH ₃	CH ₃	propargyl	CH ₂ O	2-Cl-5-CHF ₂ O-phenyl	Viscous liquid
40	138	CH ₃	CH ₃	H	CH ₂ O	5-Cl-2-CHF ₂ O-phenyl	White crystal
	139	CH ₃	CH ₃	CH ₂ OCH ₃	CH ₂ O	5-Cl-2-CHF ₂ O-phenyl	Viscous liquid
	140	CH ₃	CH ₃	propargyl	CH ₂ O	5-Cl-2-CHF ₂ O-phenyl	Viscous liquid
45	141	CH ₃	CH ₃	H	CH ₂ O	2,5-(CHF ₂ O) ₂ -phenyl	White crystal
	142	CH ₃	CH ₃	CH ₂ OCH ₃	CH ₂ O	2,5-(CHF ₂ O) ₂ -phenyl	Viscous liquid
	143	CH ₃	CH ₃	propargyl	CH ₂ O	2,5-(CHF ₂ O) ₂ -phenyl	Viscous liquid
50	144	CH ₃	CH ₃	propargyl	CH ₂ O	2,4-(CHF ₂ O) ₂ -phenyl	Viscous liquid
	145	CH ₃	CH ₃	H	CH ₂ O	3-PhO-phenyl	White crystal

Table 1 (Continued)

5	146	CH ₃	CH ₃	CH ₂ OCH ₃	CH ₂ O	3-PhO-phenyl	Viscous liquid
	147	CH ₃	CH ₃	propargyl	CH ₂ O	3-PhO-phenyl	Viscous liquid
	148	CH ₃	CH ₃	propargyl	CH ₂ O	2-CF ₃ -phenyl	Viscous liquid
10	149	CH ₃	CH ₃	CH ₂ OCH ₃	CH ₂ O	3-CF ₃ -phenyl	Viscous liquid
	150	CH ₃	CH ₃	propargyl	CH ₂ O	4-CF ₃ -phenyl	Viscous liquid
	151	CH ₃	CH ₃	CH ₂ OCH ₃	CH ₂ O	2,5-(CF ₃) ₂ -phenyl	Viscous liquid
15	152	CH ₃	CH ₃	propargyl	CH ₂ O	2,5-(CF ₃) ₂ -phenyl	Viscous liquid
	153	CH ₃	CH ₃	CH ₂ OCH ₃	CH ₂ O	3,5-(CF ₃) ₂ -phenyl	Viscous liquid
	154	CH ₃	CH ₃	propargyl	CH ₂ O	3,5-(CF ₃) ₂ -phenyl	Viscous liquid
20	155	CH ₃	CH ₃	propargyl	CH ₂ O	3-benzyloxy-phenyl	Viscous liquid
	156	CH ₃	CH ₃	propargyl	CH ₂ O	2-naphthyl	Viscous liquid
	157	CH ₃	CH ₃	CH ₂ OCH ₃	CH ₂ O	2-naphthyl	Viscous liquid
25	158	CH ₃	CH ₃	propargyl	CH ₂ O	3-naphthyl	Viscous liquid
	159	CH ₃	CH ₃	CH ₂ OCH ₃	CH ₂ O	3-naphthyl	Viscous liquid
	160	CH ₃	CH ₃	propargyl	CH ₂ O	2,2-Me ₂ -dihydrobenzofuran-5-yl	Viscous liquid
30	161	CH ₃	CH ₃	H	CH ₂ ON=C(CH ₃)	phenyl	White crystal
	162	CH ₃	CH ₃	CH ₂ OCH ₃	CH ₂ ON=C(CH ₃)	phenyl	Viscous liquid
	163	CH ₃	CH ₃	propargyl	CH ₂ ON=C(CH ₃)	phenyl	Viscous liquid
	164	CH ₃	CH ₃	H	CH ₂ ON=C(CH ₃)	3-CF ₃ -phenyl	White crystal
35	165	CH ₃	CH ₃	CH ₂ OCH ₃	CH ₂ ON=C(CH ₃)	3-CF ₃ -phenyl	Viscous liquid
	166	CH ₃	CH ₃	propargyl	CH ₂ ON=C(CH ₃)	3-CF ₃ -phenyl	Viscous liquid
	167	CH ₃	CH ₃	H	CH ₂ ON=C(CH ₃)	4-CF ₃ -phenyl	White crystal
40	168	CH ₃	CH ₃	CH ₂ OCH ₃	CH ₂ ON=C(CH ₃)	4-CF ₃ -phenyl	Viscous liquid
	169	CH ₃	CH ₃	propargyl	CH ₂ ON=C(CH ₃)	4-CF ₃ -phenyl	Viscous liquid
	170	CH ₃	CH ₃	H	CH ₂ ON=C(CH ₃)	3-Cl-phenyl	White crystal
45	171	CH ₃	CH ₃	propargyl	CH ₂ ON=C(CH ₃)	3-Cl-phenyl	Viscous liquid
	172	CH ₃	CH ₃	H	CH ₂ ON=C(CH ₃)	4-Cl-phenyl	White crystal
	173	CH ₃	CH ₃	propargyl	CH ₂ ON=C(CH ₃)	4-Cl-phenyl	Viscous liquid
50	174	CH ₃	CH ₃	H	CH ₂ ON=C(CH ₃)	3-CHF ₂ O-phenyl	White crystal
	175	CH ₃	CH ₃	propargyl	CH ₂ ON=C(CH ₃)	3-CHF ₂ O-phenyl	Viscous liquid

Table 1 (Continued)

5	176	CH ₃	CH ₃	H	CH ₂ ON=C(CH ₃)	4-CHF ₂ O-phenyl	White crystal
	177	CH ₃	CH ₃	propargyl	CH ₂ ON=C(CH ₃)	4-CHF ₂ O-phenyl	Viscous liquid
	178	CH ₃	CH ₃	H	CH ₂ ON=C(CH ₃)	3-MeO-4-CHF ₂ O-phenyl	White crystal
10	179	CH ₃	CH ₃	propargyl	CH ₂ ON=C(CH ₃)	3-MeO-4-CHF ₂ O-phenyl	Viscous liquid
	180	CH ₃	CH ₃	H	CH ₂ ON=C(CH ₃)	3-Me-4-CHF ₂ O-phenyl	White crystal
	181	CH ₃	CH ₃	propargyl	CH ₂ ON=C(CH ₃)	3-Me-4-CHF ₂ O-phenyl	Viscous liquid
15	182	CH ₃	CH ₃	H	CH ₂ ON=C(CH ₃)	3-Cl-4-CHF ₂ O-phenyl	White crystal
	183	CH ₃	CH ₃	propargyl	CH ₂ ON=C(CH ₃)	3-Cl-4-CHF ₂ O-phenyl	Viscous liquid
	184	CH ₃	CH ₃	propargyl	CH ₂ ON=C(CH ₃)	2-naphthyl	Viscous liquid
20	185	CH ₃	CH ₃	propargyl	CH ₂ ON=C(CH ₃)	3-CF ₃ O-phenyl	Viscous liquid
	186	CH ₃	CH ₃	propargyl	CH ₂ ON=C(CH ₃)	4-CF ₃ O-phenyl	Viscous liquid
	187	CH ₃	CH ₃	propargyl	CH ₂ ON=C(CH ₃)	3-MeS-phenyl	Viscous liquid
	188	CH ₃	C ₂ H ₅	propargyl	CH ₂ ON=C(CH ₃)	3-CF ₃ -phenyl	Viscous liquid
25	189	CH ₃	H	propargyl	CH ₂ ON=C(CH ₃)	3-CF ₃ -phenyl	Viscous liquid
	190	C ₂ H ₅	CH ₃	propargyl	CH ₂ ON=C(CH ₃)	3-CF ₃ -phenyl	Viscous liquid
	191	CH ₃	CH ₃	H	CH=NOCH(CH ₃)	phenyl	White crystal
30	192	CH ₃	CH ₃	CH ₂ OCH ₃	CH=NOCH(CH ₃)	phenyl	Viscous liquid
	193	CH ₃	CH ₃	propargyl	CH=NOCH(CH ₃)	phenyl	Viscous liquid
	194	CH ₃	CH ₃	H	CH=NOCH(CH ₃)	3-CF ₃ -phenyl	White crystal
35	195	CH ₃	CH ₃	CH ₂ OCH ₃	CH=NOCH(CH ₃)	3-CF ₃ -phenyl	Viscous liquid
	196	CH ₃	CH ₃	propargyl	CH=NOCH(CH ₃)	3-CF ₃ -phenyl	Viscous liquid
	197	CH ₃	CH ₃	H	CH=NOCH(CH ₃)	4-CF ₃ -phenyl	White crystal
40	198	CH ₃	CH ₃	CH ₂ OCH ₃	CH=NOCH(CH ₃)	4-CF ₃ -phenyl	Viscous liquid
	199	CH ₃	CH ₃	propargyl	CH=NOCH(CH ₃)	4-CF ₃ -phenyl	Viscous liquid
	200	CH ₃	CH ₃	H	CH=NOCH(CH ₃)	3-Cl-phenyl	White crystal
45	201	CH ₃	CH ₃	propargyl	CH=NOCH(CH ₃)	3-Cl-phenyl	Viscous liquid
	202	CH ₃	CH ₃	H	CH=NOCH(CH ₃)	4-Cl-phenyl	White crystal
	203	CH ₃	CH ₃	propargyl	CH=NOCH(CH ₃)	4-Cl-phenyl	Viscous liquid
50	204	CH ₃	CH ₃	H	CH=NOCH(CH ₃)	3-CHF ₂ O-phenyl	White crystal
	205	CH ₃	CH ₃	propargyl	CH=NOCH(CH ₃)	3-CHF ₂ O-phenyl	Viscous liquid

55

Table 1 (Continued)

5	206	CH ₃	CH ₃	H	CH=NOCH(CH ₃)	4-CHF ₂ O-phenyl	White crystal
	207	CH ₃	CH ₃	propargyl	CH=NOCH(CH ₃)	4-CHF ₂ O-phenyl	Viscous liquid
	208	CH ₃	CH ₃	H	CH=NOCH(CH ₃)	3-MeO-4-CHF ₂ O-phenyl	White crystal
10	209	CH ₃	CH ₃	propargyl	CH=NOCH(CH ₃)	3-MeO-4-CHF ₂ O-phenyl	Viscous liquid
	210	CH ₃	CH ₃	H	CH=NOCH(CH ₃)	3-Me-4-CHF ₂ O-phenyl	White crystal
	211	CH ₃	CH ₃	propargyl	CH=NOCH(CH ₃)	3-Me-4-CHF ₂ O-phenyl	Viscous liquid
15	212	CH ₃	CH ₃	H	CH=NOCH(CH ₃)	3-Cl-4-CHF ₂ O-phenyl	White crystal
	213	CH ₃	CH ₃	propargyl	CH=NOCH(CH ₃)	3-Cl-4-CHF ₂ O-phenyl	Viscous liquid
	214	CH ₃	CH ₃	propargyl	CH=NOCH(CH ₃)	2-naphthyl	Viscous liquid
20	215	CH ₃	CH ₃	propargyl	CH=NOCH(CH ₃)	3-CF ₃ O-phenyl	Viscous liquid
	216	CH ₃	CH ₃	propargyl	CH=NOCH(CH ₃)	4-CF ₃ O-phenyl	Viscous liquid
	217	CH ₃	CH ₃	propargyl	CH=NOCH(CH ₃)	3-MeS-phenyl	Viscous liquid
	218	CH ₃	CH ₃	propargyl	CH=NOCH ₂	3-CF ₃ -phenyl	Viscous liquid
25	219	CH ₃	H	propargyl	CH=NOCH(CH ₃)	3-CF ₃ -phenyl	Viscous liquid
	220	CH ₃	C ₂ H ₅	propargyl	CH=NOCH(CH ₃)	3-CF ₃ -phenyl	Viscous liquid
	221	CH ₃	CH ₃	H	CH ₂ S	phenyl	White crystal
30	222	CH ₃	CH ₃	propargyl	CH ₂ S	phenyl	Viscous liquid
	223	CH ₃	CH ₃	H	CH ₂ S	2,5-Cl ₂ phenyl	White crystal
	224	CH ₃	CH ₃	propargyl	CH ₂ S	2,5-Cl ₂ phenyl	Viscous liquid
35	225	CH ₃	CH ₃	H	CH ₂ S	2-Cl-5-CHF ₂ O-phenyl	White crystal
	226	CH ₃	CH ₃	propargyl	CH ₂ S	2-Cl-5-CHF ₂ O-phenyl	Viscous liquid
	227	CH ₃	CH ₃	propargyl	CH ₂ S	4-CF ₃ -pyridin-2-yl	Viscous liquid
40	228	CH ₃	CH ₃	H	CH ₂ S	6-Cl-4-CF ₃ -pyridin-2-yl	Viscous liquid
	229	CH ₃	CH ₃	propargyl	CH ₂ S	6-Cl-4-CF ₃ -pyridin-2-yl	Viscous liquid
	230	CH ₃	CH ₃	H	CH ₂ S	benzothiazol-2-yl	White crystal
45	231	CH ₃	CH ₃	H	C≡C	3-CF ₃ -Phenyl	White crystal
	232	CH ₃	CH ₃	propargyl	C≡C	3-CF ₃ -Phenyl	Viscous liquid
	233	CH ₃	CH ₃	CH ₂ OCH ₃	C≡C	3-CF ₃ -Phenyl	Viscous liquid
	234	CH ₃	CH ₃	propargyl	CH=CH	Phenyl	Viscous liquid
50	235	CH ₃	CH ₃	CH ₂ OCH ₃	CH=CH	Phenyl	Viscous liquid

In Table 1, Me indicates a methyl group and Ph indicates a phenyl group.

The value obtained in the analysis of the resulting compound by means of ¹H-NMR is as follows.

¹H-NMR data (CDCl₃) of the compound No. 21; 2.13 (3H, s), 3.59 (3H, s), 3.72 (3H, s), 4.95 (2H, s), 5.72 (1H, brs), 7.35 (5H, brs)

¹H-NMR data (CDCl₃) of the compound No. 22; 2.14 (3H, s), 3.6 (3H, s), 3.65 (3H, brs), 3.72 (3H, s), 4.4

- (2H, brs), 4.95 (2H, s), 5.72 (1H, brs), 7.35 (5H, brs)
¹H-NMR data (CDCl₃) of the compound No. 23; 2.23 (3H, s), 2.24 (1H, dd), 3.62 (3H, s), 3.67 (3H, s), 3.93 (1H, dd), 4.63 (1H, dd), 4.85 (2H, s), 7.34 (5H, m)
- ¹H-NMR data (CDCl₃) of the compound No. 36; 2.19 (3H, s), 3.64 (3H, s), 3.76 (3H, s), 4.95 (2H, s), 6.07 (1H, brs), 7.22 (1H, dd), 7.33 (1H, d), 7.53 (1H, d)
- ¹H-NMR data (CDCl₃) of the compound No. 37; 1.85 (3H, t), 2.19 (3H, s), 3.64 (3H, s), 3.76 (3H, s), 4.7 (2H, br), 4.95 (2H, s), 7.22 (1H, dd), 7.33 (1H, d), 7.53 (1H, d)
- ¹H-NMR data (CDCl₃) of the compound No. 38; 2.2 (3H, s), 3.55 (3H, s), 3.6 (3H, brs), 3.70 (3H, s), 4.12 (1H, dd), 4.65 (1H, dd), 4.92 (2H, s), 7.23 (1H, d), 7.31 (1H, d), 7.50 (1H, s)
- ¹H-NMR data (CDCl₃) of the compound No. 40; 2.21 (3H, s), 2.27 (1H, dd), 3.64 (3H, s), 3.70 (3H, s), 4.12 (1H, dd), 4.65 (1H, dd), 4.92 (2H, s), 7.23 (1H, d), 7.31 (1H, d), 7.50 (1H, s)
- ¹H-NMR data (CDCl₃) of the compound No. 48; 2.18 (3H, s), 2.30 (3H, s), 2.34 (3H, s), 3.59 (3H, s), 3.72 (3H, s), 4.83 (2H, s), 6.55 (1H, brs), 7.0-7.2 (3H, m)
- ¹H-NMR data (CDCl₃) of the compound No. 50; 2.17 (3H, s), 2.24 (1H, dd), 2.31 (3H, s), 2.33 (3H, s), 3.64 (3H, s), 3.70 (3H, s), 3.89 (1H, d), 4.88 (1H, d), 4.79 (1H, d), 4.86 (1H, d), 7.08 (3H, m)
- ¹H-NMR data (CDCl₃) of the compound No. 65; 2.18 (3H, s), 3.63 (3H, s), 3.73 (3H, s), 4.97 (2H, s), 6.09 (1H, brs), 6.52 (1H, t), 7.05 (1H, dd), 7.30 (1H, d), 7.38 (1H, d)
- ¹H-NMR data (CDCl₃) of the compound No. 66; 2.19 (3H, s), 3.39 (3H, s), 3.61 (3H, s), 3.71 (3H, brs), 4.74 (1H, d), 4.93 (2H, s), 5.03 (1H, d), 6.52 (1H, t), 7.04 (1H, dd), 7.31 (1H, d), 7.36 (1H, d)
- ¹H-NMR data (CDCl₃) of the compound No. 67; 2.20 (3H, s), 2.26 (1H, t), 3.64 (3H, s), 3.69 (3H, brs), 4.08 (1H, dd), 4.62 (1H, dd), 4.88 (2H, s), 6.48 (1H, t), 7.09 (1H, dd), 7.32 (1H, d), 7.50 (1H, d)
- ¹H-NMR data (CDCl₃) of the compound No. 68; 2.17 (3H, s), 3.62 (3H, s), 3.74 (3H, s), 4.90 (2H, s), 6.09 (1H, brs), 6.46 (1H, t), 7.09 (1H, d), 7.31 (1H, dd), 7.50 (1H, d)
- ¹H-NMR data (CDCl₃) of the compound No. 69; 2.18 (3H, s), 3.39 (3H, s), 3.61 (3H, s), 3.73 (3H, brs), 4.70 (1H, d), 4.87 (2H, s), 5.03 (1H, d), 6.47 (1H, t), 7.09 (1H, d), 7.31 (1H, dd), 7.50 (1H, d)
- ¹H-NMR data (CDCl₃) of the compound No. 70; 2.19 (3H, s), 2.26 (1H, t), 3.63 (3H, s), 3.70 (3H, brs), 4.08 (1H, dd), 4.62 (1H, dd), 4.88 (2H, s), 6.48 (1H, t), 7.09 (1H, d), 7.32 (1H, dd), 7.50 (1H, d)
- ¹H-NMR data (CDCl₃) of the compound No. 71; 2.17 (3H, s), 3.62 (3H, s), 3.74 (3H, s), 4.90 (2H, s), 6.09 (1H, brs), 6.46 (1H, t), 6.53 (1H, t), 7.09 (1H, d), 7.31 (1H, dd), 7.50 (1H, d)
- ¹H-NMR data (CDCl₃) of the compound No. 72; 2.18 (3H, s), 3.39 (3H, s), 3.61 (3H, s), 3.73 (3H, brs), 4.70 (1H, d), 4.87 (2H, s), 5.03 (1H, d), 6.47 (1H, t), 6.56 (1H, t), 7.09 (1H, d), 7.31 (1H, dd), 7.50 (1H, d)
- ¹H-NMR data (CDCl₃) of the compound No. 73; 2.19 (3H, s), 2.26 (1H, t), 3.63 (3H, s), 3.70 (3H, brs), 4.08 (1H, dd), 4.62 (1H, dd), 4.88 (2H, s), 6.48 (1H, t), 6.56 (1H, t), 7.09 (1H, d), 7.32 (1H, dd), 7.50 (1H, d)
- ¹H-NMR data (CDCl₃) of the compound No. 75; 1.13 (3H, t), 2.08 (3H, s), 3.54 (3H, s), 3.60 (2H, br), 3.61 (3H, brs), 4.75 (1H, d), 4.82 (1H, d), 6.9-7.2 (6H, m), 7.3-7.4 (3H, m)
- ¹H-NMR data (CDCl₃) of the compound No. 76; 2.10 (3H, s), 3.37 (3H, s), 3.67 (3H, brs), 4.63 (1H, d), 4.80 (2H, s), 5.04 (1H, d), 6.95-7.16 (6H, m), 7.3-7.4 (3H, m)
- ¹H-NMR data (CDCl₃) of the compound No. 77; 2.11 (3H, s), 2.22 (1H, t), 3.62 (3H, s), 3.65 (3H, brs), 3.96 (1H, dd), 4.63 (1H, dd), 4.81 (2H, s), 6.92-7.18 (6H, m), 7.3-7.4 (3H, m)
- ¹H-NMR data (CDCl₃) of the compound No. 116; 2.14 (3H, s), 2.25 (3H, s), 2.26 (3H, s), 3.69 (3H, s), 3.75 (3H, s), 4.78 (2H, s), 6.25 (1H, brs), 6.80 (1H, d), 6.96 (2H, m)
- ¹H-NMR data (CDCl₃) of the compound No. 117; 2.13 (3H, s), 2.23 (1H, t), 2.26 (3H, s), 2.27 (3H, s), 3.68 (3H, brs), 3.71 (3H, s), 4.16 (1H, brd), 4.62 (1H, brd), 4.74 (2H, d), 6.78 (1H, d), 6.95 (1H, d), 6.96 (1H, s)
- ¹H-NMR data (CDCl₃) of the compound No. 164; 2.28 (3H, s), 2.33 (3H, s), 3.6 (3H, s), 3.7 (3H, s), 4.78 (2H, s), 6.2 (1H, brs), 7.2-7.8 (4H, m)
- ¹H-NMR data (CDCl₃) of the compound No. 165; 2.20 (3H, s), 2.32 (3H, s), 3.70 (6H, s), 3.75 (3H, brs), 4.22 (1H, dd), 4.75 (1H, dd), 4.94 (1H, d), 5.02 (1H, d), 7.48 (1H, t), 7.60 (1H, d), 7.79 (1H, d), 7.88 (1H, s)
- ¹H-NMR data (CDCl₃) of the compound No. 166; 2.20 (3H, s), 2.26 (1H, d), 2.32 (3H, s), 3.70 (6H, s), 4.22 (1H, dd), 4.75 (1H, dd), 4.94 (1H, d), 5.02 (1H, d), 7.48 (1H, t), 7.60 (1H, d), 7.79 (1H, d), 7.88 (1H, s)
- ¹H-NMR data (CDCl₃) of the compound No. 167; 2.21 (3H, s), 2.28 (3H, s), 3.69 (3H, s), 3.79 (3H, s), 4.95 (2H, s), 7.64 (2H, d), 7.71 (2H, d)
- ¹H-NMR data (CDCl₃) of the compound No. 169; 2.20 (3H, d), 2.27 (1H, t), 2.32 (3H, s), 3.70 (6H, brs), 4.23 (1H, dd), 4.77 (1H, dd), 4.94 (1H, d), 5.03 (1H, d), 7.61 (2H, d), 7.73 (2H, d)
- ¹H-NMR data (CDCl₃) of the compound No. 194; 1.58 (3H, d), 2.21 (3H, s), 3.69 (3H, s), 5.23 (1H, q), 7.08 (1H, brs), 7.4-7.6 (4H, m), 8.01 (1H, s)
- ¹H-NMR data (CDCl₃) of the compound No. 196; 1.58 (3H, d), 2.18 (1H, dd), 2.26 (3H, s), 3.68 (3H, s), 3.90 (1H, dd), 4.5 (1H, dd), 5.22 (1H, q), 7.4-7.6 (4H, m), 7.97 (1H, d)

¹H-NMR data (CDCl₃) of the compound No. 197; 1.57 (3H, d), 2.21 (3H, s), 3.68 (3H, s), 3.69 (3H, s), 5.25 (1H, q), 7.08 (1H, brs), 7.46 (2H, d), 7.61 (2H, d), 8.01 (1H, s)

¹H-NMR data (CDCl₃) of the compound No. 199; 1.56 (3H, d), 2.20 (1H, dd), 2.25 (3H, s), 3.68 (6H, brs), 4.52 (1H, dd), 5.22 (1H, q), 7.45 (2H, m), 7.6 (2H, m), 7.96 (1H, s)

5 ¹H-NMR data (CDCl₃) of the compound No. 228; 2.27 (3H, s), 3.68 (3H, s), 3.83 (3H, s), 4.14 (2H, s), 5.5 (1H, brs), 7.77 (1H, d), 8.63 (1H, d)

¹H-NMR data (CDCl₃) of the compound No. 229; 2.35 (3H, s), 2.48 (1H, d), 3.94 (1H, d), 4.10 (3H, s), 4.12 (3H, s), 4.58 (1H, d), 4.94 (2H, s), 7.75 (1H, s), 8.62 (1H, s)

10 ¹H-NMR data (CDCl₃) of the compound No. 230; 2.25 (3H, s), 3.67 (3H, s), 3.91 (3H, s), 4.24 (2H, s), 7.32 (1H, t), 7.47 (1H, t), 7.74 (1H, d), 8.02 (1H, d), 9.6 (1H, brs)

¹H-NMR data (CDCl₃) of the compound No. 231; 2.33 (3H, s), 3.73 (3H, s), 3.83 (3H, s), 6.35 (1H, brs), 7.46 (1H, t), 7.56 (1H, d), 7.63 (1H, d), 7.72 (1H, s)

¹H-NMR data (CDCl₃) of the compound No. 232; 2.27 (1H, t), 2.35 (3H, s), 3.71 (3H, s), 3.79 (3H, brs), 4.25 (1H, d), 4.85 (1H, d), 7.46 (1H, t), 7.56 (1H, d), 7.61 (1H, d), 7.70 (1H, s)

15 ¹H-NMR data (CDCl₃) of the compound No. 233; 2.34 (3H, s), 3.46 (3H, s), 3.69 (3H, s), 3.80 (3H, brs), 4.89 (1H, d), 5.25 (1H, d), 7.45 (1H, t), 7.54 (1H, d), 7.60 (1H, d), 7.69 (1H, s)

Formulation Example 1

20 20 Parts of the compound No. 2 described in Table 1, 75 parts of diatomaceous earth and 5 parts of a surfactant containing alkylbenzenesulfonic acid as a main ingredient were uniformly pulverized and mixed to give a wettable powder.

Formulation Example 2

25 30 Parts of the compound No. 3 described in Table 1, 15 parts of "Sorpil" 3005X (trade mark of Toho Kagaku Co., Ltd., mixture of nonionic surfactant and anionic surfactant), 25 parts of xylene and 30 parts of dimethylformamide were sufficiently mixed to give an emulsifiable concentrate.

30 The following Test Examples illustrate that the compound of the present invention is useful as an agricultural/horticultural fungicide

Test Example 1 Preventive activity on wheat powdery mildew

35 Wettable powders prepared according to the same manner as that described in Formulation Example 1 were diluted with water to the predetermined concentration and then applied by foliar application on wheat plants (var. Norin No. 61) at the 1 to 2 leaf stage grown in pots of 6 cm in diameter at a ratio of 10 ml per one pot. After the chemical solution was air-dried, a spore suspension obtained from the leaf of wheat infected with *Erysiphe graminis* was spray-inoculated. After inoculation, the seedling of wheat was allowed to stand at room temperature for 7 to 10 days.

40 For evaluation, the diseased area ratio of each leaf was measured and the preventive value was calculated from the following equation:

The preventive value (%) =

$$45 \frac{(\text{average diseased area ratio in untreated plot}) - (\text{average diseased area ratio in treated plot})}{(\text{average diseased area ratio in untreated plot})} \times 100$$

50 The results are shown in the column under the item "preventive value 1" in Table 2.
The test compound No. cited in the Table 2 corresponds to the compound No. of Table 1.

Test Example 2 Preventive activity on wheat brown

55 Wettable powders prepared according to the same manner as that described in Formulation Example 1 were diluted with water to the predetermined concentration and then applied by foliar application on wheat plants (var. Norin No. 61) at the 1 to 2 leaf stage grown in pots of 6 cm in diameter at a ratio of 10 ml per

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one pot. After the chemical solution was air-dried, a spore suspension obtained by pulverizing the leaf of wheat infected with *Puccinia recondita* was spray-inoculated. After inoculation, the wheat seedling was maintained in a moist chamber at 22°C for 15 hours and was allowed to stand on a water tank in a greenhouse for 7 days.

- 5 For evaluation, the diseased area ratio of each leaf was measured and the preventive value was calculated from the following equation:

The preventive value (%) =

10

$$\frac{(\text{average diseased area ratio in untreated plot}) - (\text{average diseased area ratio in treated plot})}{(\text{average diseased area ratio in untreated plot})} \times 100$$

15

The results are shown in the column under the item "preventive value 2" in Table 2.

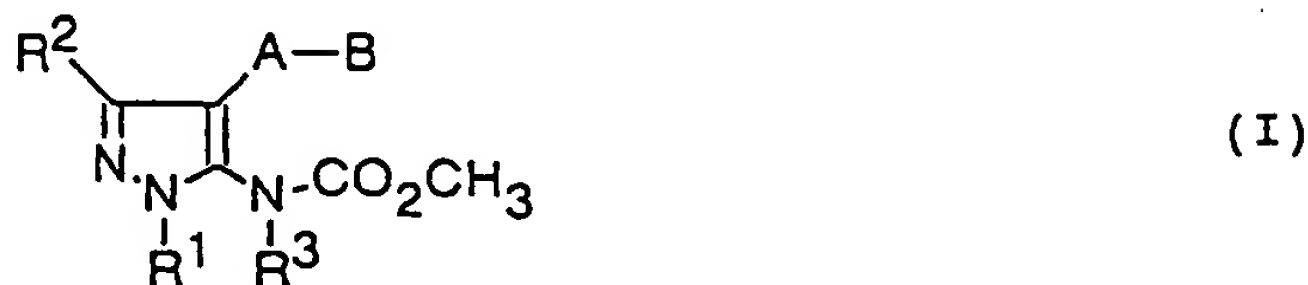
Table 2

20

Test compound No.	Concentration of active ingredient (ppm)	Preventive value 1 (%)	Preventive value 2 (%)
22	200	91	87
25 23	200	100	100
37	200	98	92
38	200	100	100
30 40	200	100	100
48	200	93	86
50	200	100	100
35 66	200	100	100
67	200	100	100
69	200	100	100
70	200	100	100
40 72	200	100	100
73	200	100	100
76	200	99	98
45 77	200	100	100
117	200	95	96
165	200	100	100
50 166	200	100	100
169	200	100	100
196	200	100	100
199	200	100	100
55 230	200	89	85
232	200	100	100

Claims

1. A N-pyrazolyl carbamate derivative represented by the general formula (I):



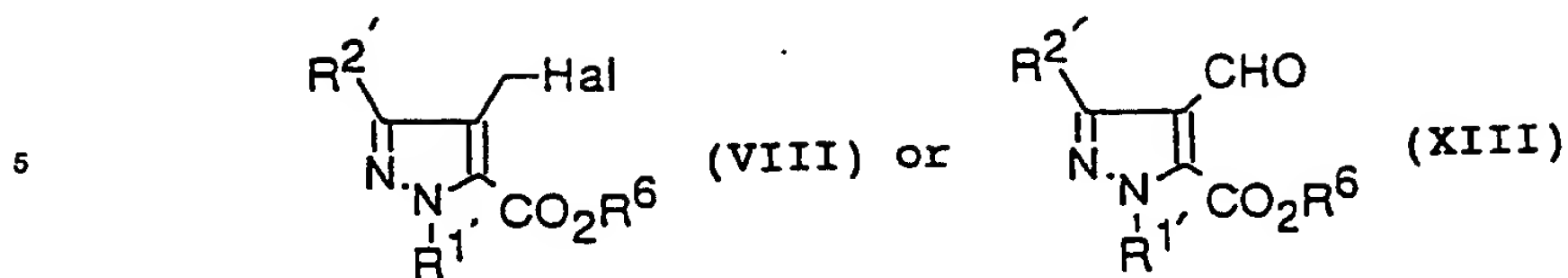
wherein R¹ and R² independently indicate a hydrogen atom or a C₁-C₄ alkyl group; R³ is a hydrogen atom, a C₁-C₄ alkyl group, a C₂-C₅ alkynyl group, a C₂-C₄ alkylthioalkyl group or a C₂-C₄ alkoxyalkyl group; A is -O-, -C(O)-, -OCH₂-, -CH₂O-, -CH₂S-, -C≡C-, -CH=CH-, -CH₂CH₂-, -CH₂ON=C(R⁴)- or -CH=NOC(R⁴)(R⁵)- (wherein R⁴ and R⁵ independently indicate a hydrogen atom or a C₁-C₄ alkyl group); and B is a hydrogen atom, an optionally substituted aryl group or an optionally substituted heterocyclic group.

2. The N-pyrazolyl carbamate derivative according to claim 1, wherein R¹ and R² indicate a C₁-C₄ alkyl group; R³ is a hydrogen atom, a C₁-C₄ alkyl group, a C₂-C₅ alkynyl group or a C₂-C₄ alkoxyalkyl group; A is -O-, -OCH₂-, -CH₂O-, -CH₂S-, -C≡C-, -CH=CH-, -CH₂ON=C(R⁴)- or -CH=NOC(R⁴)(R⁵)- (wherein R⁴ and R⁵ independently indicate a hydrogen atom or a C₁-C₄ alkyl group); and B is an aryl group or a heterocyclic group which may be substituted with a substituent(s) selected from a group consisting of a cyano group, a nitro group, a halogen atom, a C₁-C₄ alkyl group, a C₁-C₄ haloalkyl group, a C₁-C₆ alkoxy group which may be substituted with a halogen atom or a C₃-C₆ cycloalkyl group, a C₁-C₆ alkylthio group, a C₂-C₆ alkenyloxy group which may be substituted with a halogen atom, a C₂-C₆ alkynyloxy group and a phenoxy, benzyloxy or pyridyloxy group which may be substituted by the cyano group, nitro group, halogen atom, C₁-C₄ alkyl group, C₁-C₄ haloalkyl group, C₁-C₆ alkoxy group which may be substituted with a halogen atom or a C₃-C₆ cycloalkyl group, C₁-C₆ alkylthio group, C₂-C₆ alkenyloxy group which may be substituted with a halogen atom or C₂-C₆ alkynyloxy group.

3. The N-pyrazolyl carbamate derivative according to claim 1, wherein R¹ and R² indicate a C₁-C₄ alkyl group; R³ is a hydrogen atom, a C₁-C₄ alkyl group, a C₂-C₅ alkynyl group or a C₂-C₄ alkoxyalkyl group; A is -O-, -OCH₂-, -CH₂O-, -CH₂S-, -C≡C-, -CH₂ON=C(R⁴)- or -CH=NOC(R⁴)(R⁵)- (wherein R⁴ and R⁵ independently indicate a hydrogen atom or a C₁-C₂ alkyl group); and B is an aryl group or a heterocyclic group which may contain a substituent(s) selected from a halogen atom, a C₁-C₄ alkyl group, a C₁-C₄ haloalkyl group, a C₁-C₆ alkoxy group which may be substituted with a halogen atom and a phenoxy group.

4. The N-pyrazolyl carbamate derivative according to claim 1, wherein R¹ and R² indicate a methyl group; R³ is a hydrogen atom, a C₁-C₄ alkyl group, a C₂-C₅ alkynyl group or a C₂-C₄ alkoxyalkyl group; A is -OCH₂-, -CH₂O-, -CH₂S-, -C≡C-, -CH₂ON=C(R⁴)- or -CH=NOC(R⁴)(R⁵)- (wherein R⁴ is a hydrogen atom or a methyl group and R⁵ is a hydrogen atom); and B is a phenyl group which may contain a substituent(s) selected from a group consisting of halogen atom, a C₁-C₄ alkyl group, a C₁-C₄ alkoxy group which may be substituted with a fluorine atom, a trifluoromethyl group and a phenoxy group.

5. A pyrazole-5-yl carboxylate derivative represented by the general formula:



10 wherein $R^{1'}$ and $R^{2'}$ indicate a C_1 - C_4 alkyl group; Hal is a chlorine atom or a bromine atom; and R^6 is a C_1 - C_4 alkyl group as an intermediate for the production of the N-pyrazolyl carbamate derivative of claim 2 or 3.

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6. The 1,3-dimethylpyrazole-5-yl carboxylate derivative according to claim 5, wherein $R^{1'}$ and $R^{2'}$ indicate a methyl group.
 7. An agricultural/horticultural fungicide comprising the N-pyrazolyl carbamate derivative of claim 1 as an active ingredient.
 - 20 8. An agricultural/horticultural fungicide comprising the N-pyrazolyl carbamate derivative of claim 2 as an active ingredient.
 9. An agricultural/horticultural fungicide comprising the N-pyrazolyl carbamate derivative of claim 3 as an active ingredient.
 - 25 10. An agricultural/horticultural fungicide comprising the N-pyrazolyl carbamate derivative of claim 4 as an active ingredient.

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EUROPEAN SEARCH REPORT

Application Number
EP 94 11 9428

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
A	EP-A-0 571 326 (SANDOZ LTD ET AL.) * page 2 - page 3, line 24 * ---	1,7	C07D231/18 C07D231/38 A01N43/56
A	EP-A-0 483 851 (MITSUBISHI KASEI CORPORATION) * the whole document * ---	1,7	
A	EP-A-0 433 899 (MITSUBISHI KASEI CORPORATION) * the whole document * D & JP-A-4 217 668 (...) ---	1,7	
A,D	EP-A-0 129 830 (SDS BIOTECH K.K.) * the whole document * ---	1,7	
A	PATENT ABSTRACTS OF JAPAN vol. 17, no. 644 (C-1134) (6273) 30 November 1993 & JP-A-05 201 980 (MITSUBISHI KASEI CORPORATION) 10 August 1993 * abstract * -----	1,7	
			TECHNICAL FIELDS SEARCHED (Int.Cl.6)
			C07D
The present search report has been drawn up for all claims			
Place of search BERLIN		Date of completion of the search 14 March 1995	Examiner Kyriakakou, G
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application I : document cited for other reasons ----- & : member of the same patent family, corresponding document			

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